

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

JP 05295161

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

 CLAIMS
 

---

[Claim(s)]

[Claim 1] In the solution of the thermoplastic polymer which dissolved in the styrene system monomer or the hydrocarbon system solvent A styrene system monomer \*\* React with the catalyst \*\* (A) transition-metals compound and (C) this transition-metals compound which use (A) transition-metals compound and (B) aluminoxane as a principal component. It reacts with the catalyst which uses as a principal component the catalyst \*\* (A) transition-metals compound which uses as a principal component the compound which forms the complex of ionicity, (B) aluminoxane, and the (D) organoaluminium compound or \*\* (A) transition-metals compound, and (C) this transition-metals compound. Or it copolymerizes and a polystyrene system resin constituent is prepared. the bottom of existence of the catalyst which uses as a principal component the compound and the (D) organoaluminium compound which form the complex of ionicity -- a polymerization -- subsequently The manufacture approach of the porosity polystyrene system ingredient characterized by processing after fabricating this resin constituent with the hydrocarbon system solvent which dissolves a thermoplastic polymer, and removing this thermoplastic polymer.

[Claim 2] A styrene system monomer is a general formula (I).

[Formula 1]



$$\cdots (I)$$

R1 shows the substituent containing any one or more sorts of a hydrogen atom, a halogen atom or a carbon atom, an oxygen atom, or the silicon atom among [type, and m shows the integer of 1-5. However, it is R1 when m is plurality. It may be the same or you may differ. ] The manufacture approach of the porosity polystyrene system ingredient according to claim 1 which comes out and is characterized by what is expressed.

[Claim 3] The manufacture approach of the porosity polystyrene system ingredient according to claim 1 or 2 characterized by a polystyrene system resin constituent containing the styrene system polymer or styrene system copolymer which has syndiotactic structure.

[Claim 4] The manufacture approach of the porosity polystyrene system ingredient according to claim 1 to 3 characterized by the content of the thermoplastic polymer in a polystyrene system resin constituent being 1 - 90 % of the weight.

---

 [Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the approach of manufacturing efficiently the porosity polystyrene system ingredient which was excellent in thermal resistance useful as porosity separation material, such as ultrafiltration membrane, an ultraprecise filtration membrane, a reverse osmotic membrane, ion exchange membrane, a gas separation membrane, and permeable membrane, and solvent resistance from the polystyrene system resin constituent which the styrene system polymer or styrene system copolymer which has syndiotactic structure, and the thermoplastic polymer distributed to homogeneity, in detail about the manufacture approach of a porosity polystyrene system ingredient.

[0002]

[Description of the Prior Art] Although the styrene system polymer manufactured by a radical polymerization method etc. from the former was fabricated by the thing of various configurations and was broadly used by the various fabricating methods as a home electric appliance, a business machine, household articles, a container, a toy, furniture, materials a synthetic paper and industrial [ other ], etc., the spacial configuration has atactic structure and there was a fault of being inferior to thermal resistance and chemical resistance.

[0003] By the way, as what canceled the fault of the styrene system polymer of such atactic structure, this invention persons' research consortium succeeded in development of the high styrene system polymer of syndiotacticity, and developed the styrene system polymer which copolymerized this styrene monomer and other components further the other day (JP,62-104818,A, 63-241009 official report). The styrene system polymer or copolymer of such syndiotactic structures is excellent in thermal resistance, chemical resistance, and electrical characteristics, and the application covering an another side is expected.

[0004] As one of the applicable fields of these, separation means, such as an ultrafiltration and reverse osmosis, have the useful fine porosity film taking advantage of the thermal resistance of syndiotactic polystyrene, hydrolytic stability, and solvent resistance. For example, the case where a vinyl aromatic series polymer is polystyrene is indicated by especially JP,2-4840,A about the micropore nature asymmetric membrane and its manufacture approach of a syndiotactic vinyl aromatic series polymer. According to this disclosure technique, it is (a). It is characterized by supercooling this solution, (c) Ranking second, forming this solution in the shape of film, and performing phase separation and pore formation after an appropriate time [ (d) ] under temperature up, so that the solution which consists of syndiotactic polystyrene and a polar nonprotic solvent may be formed and the syndiotactic polystyrene in the (b) solution may be held in the dissolution condition. However, by this approach, one polymer is dissolved once, it supercools under the conditions which can hold 2 dissolution condition, and the actuation made into the shape of film is included in 3 pans. From this, the solvent of a large quantity is needed, the technique which supercools with the dissolution condition of this polymer held, and the equipment which produces a film in addition are needed for preparation of the collected amount, and there is a still more difficult point in practical use from an economical and efficient standpoint.

[0005]

[Problem(s) to be Solved by the Invention] Then, in view of the above-mentioned actual condition, this invention persons held the crystallinity of syndiotactic polystyrene original, and this polystyrene and a specific thermoplastic polymer distributed to homogeneity highly, and they developed the good styrene resin constituent and its manufacture approach of manufacture effectiveness. Furthermore, research was wholeheartedly repeated about this newly developed styrene resin constituent that porosity separation material should be developed. Consequently, it found out that the object could be attained by carrying out the polymerization (\*\*) of the styrene system monomer, preparing a polystyrene system resin constituent, and removing a thermoplastic polymer after shaping using a specific catalyst, in the solution of the thermoplastic polymer which dissolved in the styrene system monomer or the hydrocarbon system solvent. This invention is completed based on this knowledge.

[0006]

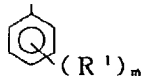
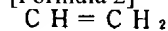
[Means for Solving the Problem] This invention namely, in the solution of the thermoplastic polymer which dissolved in the styrene system monomer or the hydrocarbon system solvent A styrene system monomer \*\* React with the catalyst \*\*(A) transition-metals compound and (C) this transition-metals compound which use (A) transition-metals compound and (B) aluminoxane as a principal component. It reacts with the catalyst which uses as a principal component the catalyst \*\*(A) transition-metals compound which uses as a principal component the compound which forms the complex of ionicity, (B) aluminoxane, and the (D) organoaluminium compound or \*\*(A) transition-metals compound, and (C) this transition-metals

compound. Or it copolymerizes and a polystyrene system resin constituent is prepared. the bottom of existence of the catalyst which uses as a principal component the compound and the (D) organoaluminium compound which form the complex of ionicity -- a polymerization -- subsequently It processes after fabricating this resin constituent with the hydrocarbon system solvent which dissolves a thermoplastic polymer, and the manufacture approach of the porosity polystyrene system ingredient characterized by removing this thermoplastic polymer is offered.

[0007] First, the styrene system monomer which can be used by the approach of this invention carries out the designation of styrene and/or the styrene derivative. Here, as a styrene system monomer which consists of a styrene derivative, although there are various kinds of things, as a desirable thing, it is a general formula (I).

[0008]

[Formula 2]



... ( I )

[0009] R1 shows the substituent containing any one or more sorts of a hydrogen atom, a halogen atom or a carbon atom, an oxygen atom, or the silicon atom among [type, and m shows the integer of 1-5. However, it is R1 when m is plurality. It may be the same or you may differ. ] It can come out and the styrene system monomer expressed can be mentioned.

[0010] It sets to the styrene system monomer expressed with this general formula (I), and is R1. Although various kinds of substituents are expressed like the above-mentioned, chlorine, a fluorine, a bromine, and iodine can be mentioned as a halogen atom here. Moreover, as an example of the substituent containing a carbon atom, there is a halogenation alkyl group of the carbon numbers 1-20, such as an alkyl group of the carbon numbers 1-20, such as a methyl group, an ethyl group, an isopropyl group, and tertiary butyl, or a chloro ethyl group, and a BUROMO ethyl group. As an example of the substituent containing a carbon atom and a silicon atom, the alkyl silyl radical of the carbon numbers 1-20, such as a trimethylsilyl radical, is mentioned further again.

[0011] As an example of this styrene system monomer, styrene, p-methyl styrene; -- o-methyl styrene; -- m-methyl styrene; -- alkyl styrene, such as 2, 4-dimethyl styrene; 2, 5-dimethyl styrene; 3, 4-dimethyl styrene; 3, and 5-dimethyl styrene; p-tertiary butyl styrene, -- p-chloro styrene; m-chloro styrene; -- o-chloro styrene; -- p-bromostyrene; -- m-bromostyrene; -- o-bromostyrene; -- p-fluoro styrene; -- m-fluoro styrene; -- o-fluoro styrene; -- halogenation styrene, such as o-methyl-p-fluoro styrene, -- 4-vinyl biphenyl; -- 3-vinyl biphenyl; -- vinyl biphenyls, such as 2-vinyl biphenyl, -- 1- (4-vinyl phenyl)-naphthalene; 2- (4-vinyl phenyl)-naphthalene; -- 1-(3-vinyl phenyl)-naphthalene; -- 2-(3-vinyl phenyl)-naphthalene; -- 1-(2-vinyl phenyl)-naphthalene; -- vinyl phenyl naphthalene, such as 2-(2-vinyl phenyl) naphthalene, -- 1- (4-vinyl phenyl)-anthracene; 2- (4-vinyl phenyl)-anthracene; 9- (4-vinyl phenyl)-anthracene; 1- (3-vinyl phenyl)-anthracene; 2- (3-vinyl phenyl)-anthracene; -- 9-(3-vinyl phenyl)-anthracene; -- 1-(2-vinyl phenyl)-anthracene; -- 2-(2-vinyl phenyl)-anthracene; -- vinyl phenyl anthracene, such as a 9-(2-vinyl phenyl)-anthracene, -- 1- (4-vinyl phenyl)-phenanthrene; 2- (4-vinyl phenyl)-phenanthrene; 3- (4-vinyl phenyl)-phenanthrene; 4- (4-vinyl phenyl)-phenanthrene; 9- (4-vinyl phenyl)-phenanthrene; 1- (3-vinyl phenyl)-phenanthrene; 2- (3-vinyl phenyl)-phenanthrene; 3- (3-vinyl phenyl)-phenanthrene; 4- (3-vinyl phenyl)-phenanthrene; 9- (3-vinyl phenyl)-phenanthrene; 1- (2-vinyl phenyl)-phenanthrene; 2- (2-vinyl phenyl)-phenanthrene; -- 3-(2-vinyl phenyl)-phenanthrene; -- 4-(2-vinyl phenyl)-phenanthrene; -- vinyl phenyl phenanthrenes, such as a 9-(2-vinyl phenyl)-phenanthrene, -- 1- (4-vinyl phenyl)-pyrene; -- 2-(4-vinyl phenyl)-pyrene; -- 1-(3-vinyl phenyl)-pyrene; -- 2-(3-vinyl phenyl)-pyrene; -- 1-(2-vinyl phenyl)-pyrene; -- vinyl phenyl pyrenes, such as a 2-(2-vinyl phenyl)-pyrene, -- 4-vinyl-p-terphenyl; 4-vinyl-m-terphenyl; 4-vinyl-o-terphenyl; -- 3-vinyl-p-terphenyl; -- 3-vinyl-m-terphenyl; -- 3-vinyl-o-terphenyl; -- 2-vinyl-p-terphenyl; -- 2-vinyl-m-terphenyl; -- vinyl terphenyl, such as 2-vinyl-o-terphenyl, -- Vinyl phenyl terphenyl, such as 4-(4-vinyl phenyl)-p-terphenyl 4-vinyl-4'-methyl biphenyl; -- 4-vinyl-3'-methyl biphenyl; -- 4-vinyl-2'-methyl biphenyl; -- 2-methyl-4-vinyl biphenyl; -- vinyl alkyl biphenyls, such as a 3-methyl-4-vinyl biphenyl, -- 4-vinyl-4'-fluoro biphenyl; 4-vinyl-3'-fluoro biphenyl; 4-vinyl-2'-fluoro biphenyl; 4-vinyl-2-fluoro biphenyl; 4-vinyl-3-fluoro biphenyl; 4-vinyl-4'-chloro biphenyl; 4-vinyl-3'-chloro biphenyl; 4-vinyl-2'-chloro biphenyl; 4-vinyl-2'-chloro biphenyl; 4-vinyl-3'-chloro biphenyl; 4-vinyl-4'-BUROMO biphenyl; -- 4-vinyl-3'-BUROMO biphenyl; -- 4-vinyl-2'-BUROMO biphenyl; -- 4-vinyl-2-BUROMO biphenyl; -- halogenation vinyl biphenyls, such as a 4-vinyl-3-BUROMO biphenyl, -- Trialkylsilyl vinyl biphenyls, such as a 4-vinyl-4'-trimethylsilyl biphenyl Trialkylsilyl methylvinyl biphenyls, such as a 4-vinyl-4'-trimethylsilylmethyl biphenyl p-chloro ethyl styrene; -- m-chloro ethyl styrene; -- halogenation alkyl styrene, such as o-chloro ethyl styrene, -- p-trimethylsilyl styrene; m-trimethylsilyl styrene; -- o-trimethylsilyl styrene; -- p-triethyl silyl styrene; -- m-triethyl silyl styrene; -- o-triethyl silyl styrene; -- alkyl silyl styrene, such as p-dimethyl tertiary-butylsilyl styrene, -- p-dimethylphenyl silyl styrene; -- p-methyl diphenyl silyl styrene; -- phenyl group content silyl styrene, such as p-triphenyl silyl styrene, -- p-dimethyl chlorosilyl styrene; -- p-methyl dichloro silyl styrene; -- p-trichlorosilyl styrene; -- p-dimethyl BUROMO silyl styrene; -- halogen content silyl styrene, such as p-dimethyl iodine silyl styrene, -- Silyl radical content silyl styrene, such as p-trimethylsilyl dimethylsilyl styrene, is mentioned. By the approach of this invention, a polymerization may be carried out using one kind of the above-mentioned styrene system monomer, or you may copolymerize using two or more sorts. By the approach of this invention, a styrene system (\*\*) polymer, especially the styrene system (\*\*) polymer which has advanced syndiotactic structure are obtained by carrying out the polymerization (\*\*) of the styrene system monomer. Furthermore, by the approach of this invention, the third component can also be added in the range which does not spoil remarkably the syndiotactic structure in the property of the styrene system

(\*\*) polymer obtained, or the chain of a repeat unit.

[0012] the styrene system monomer mentioned above by the approach of this invention -- a polymerization -- or, although it copolymerizes As a catalyst used in these polymerizations or copolymerization \*\* React with the catalyst \*\* (A) transition-metals compound and (C) this transition-metals compound which use (A) transition-metals compound and (B) aluminosilane as a principal component. It reacts with the catalyst which uses as a principal component the catalyst \*\* (A) transition-metals compound which uses as a principal component the compound which forms the complex of ionicity, (B) aluminosilane, and the (D) organoaluminum compound or \*\* (A) transition-metals compound, and (C) this transition-metals compound. It is the catalyst which uses as a principal component the compound and the (D) organoaluminum compound which form the complex of ionicity.

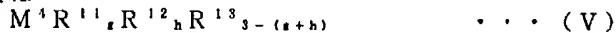
[0013] as the transition-metals compound which are introduction and the (A) component -- the periodic table IIIB, IVB, VB and VIB, and VIII, a lanthanoids group's metallic compounds -- desirable -- the metallic compounds of the periodic tables IVB and VIB and a lanthanoids group -- especially -- desirable -- the periodic table IVB a group's metallic compounds -- it is especially the compound of Ti, Zr, or Hf. (A) although there are various things as a transition-metals compound which is a component -- desirable -- the following general formula (II), (III), and (IV) -- or (V) --

[0014]

[Formula 3]



又 は



[0015] R2 -R13 show a hydrogen atom, a halogen atom, the alkyl group of carbon numbers 1-20, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the alkyl aryl radical of carbon numbers 7-20 or an arylated alkyl radical, the aryloxy group of carbon numbers 6-20, the acyloxy radical of carbon numbers 1-20, an acetyl acetonyl radical, a cyclopentadienyl group, a substituent cyclopentadienyl group, or indenyl \*\* among [type, respectively. Moreover, a, b, and c show zero or more integers with which  $0 \leq a+b+c \leq 4$  are filled, respectively, d and e show zero or more integers with which  $0 \leq d+e \leq 3$  are filled, respectively, f shows zero or more integers with which  $0 \leq f \leq 2$  is filled, and g and h show zero or more integers with which  $0 \leq g+h \leq 3$  are filled respectively. Furthermore, M1 and M2 Titanium, a zirconium, a hafnium, or vanadium is shown and it is M3 and M4. Vanadium is shown. ] They are at least one sort of compounds which came out and were chosen from the transition-metals compound expressed. Also in these transition-metals compounds, it is M1 in said general formula (II). It is desirable to use what is titanium or a zirconium.

[0016] Here, as a halogen atom, they are specifically a chlorine atom, a bromine atom, an iodine atom, or a fluorine atom among what is shown by R2 -R13 in said formula. Moreover, a substituent cyclopentadienyl group is a cyclopentadienyl group permuted by one or more alkyl groups of carbon numbers 1-6, and, specifically, are methylcyclopentadienyl radical; 1, a 2-dimethylcyclopentadienyl radical; pentamethylcyclopentadienyl group, etc. Independently R2 -R13 in said formula, respectively Moreover, a hydrogen atom, the alkyl group of carbon numbers 1-20 (-- concrete -- a methyl group, an ethyl group, a propyl group, n-butyl, an isobutyl radical, an amyl group, an isoamyl radical, an octyl radical, a 2-ethylhexyl radical, etc. --) -- The alkoxy group of carbon numbers 1-20 (-- concrete -- a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, a hexyloxy radical, an octyloxy radical, 2-ethylhexyloxy radical, etc. --) -- The aryl groups (specifically a phenyl group, a naphthyl group, etc.) of carbon numbers 6-20, the arylated alkyl radical of carbon numbers 7-20 (-- concrete -- benzyl, a phenethyl radical, 9-anthryl methyl group, etc. --) -- you may be the acyloxy radicals (specifically acetyloxy radical etc.) of carbon numbers 1-20. As long as the above-mentioned conditions are provided, these [ R2-R13 ] may be the same, or may differ.

[0017] As an example of a titanium compound, among the transition-metals compounds expressed with such said general formula (II)- (V) Tetramethoxy titanium, tetra-ethoxy titanium, a tetrapod Titanium, tetraisopropoxy titanium, a titanium tetrachloride, a titanium trichloride, a titanium dichloride, titanium hydride, cyclopentadienyl trimethyl titanium, cyclopentadienyl triethyl titanium, cyclopentadienyl TORIPURO pill titanium, (n-butoxy) Cyclopentadienyl tributyl titanium, methylcyclopentadienyl trimethyl titanium; 1, 2-dimethylcyclopentadienyl trimethyl titanium, pentamethylcyclopentadienyl trimethyl titanium, pentamethylcyclopentadienyl triethyl titanium, Pentamethylcyclopentadienyl TORIPURO pill titanium, Pentamethylcyclopentadienyl tributyl titanium, Cyclopentadienyl methyl titanium dichloride, Cyclopentadienyl ethyl titanium dichloride, pentamethylcyclopentadienyl methyl titanium dichloride, PENTAMECHIRUKU cyclopentadienyl ethyl titanium dichloride, and cyclopentadienyl dimethyl CHITAMMONO chloride; Cyclopentadienyl diethyl CHITAMMONO chloride, cyclopentadienyl titanium trimethoxide, cyclopentadienyl CHITANTORI ethoxide, cyclopentadienyl CHITANTORI propoxide, a cyclopentadienyl CHITANTORI phenoxide, Pentamethylcyclopentadienyl titanium trimethoxide, pentamethylcyclopentadienyl CHITANTORI ethoxide, pentamethylcyclopentadienyl CHITANTORI propoxide,

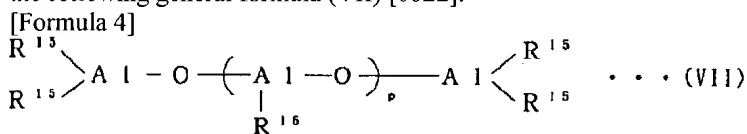
pentamethylcyclopentadienyl titanium tributoxide, A pentamethylcyclopentadienyl CHITANTORI phenoxide, cyclopentadienyl titanium trichloride, pentamethylcyclopentadienyl titanium trichloride, cyclopentadienyl methoxy titanium dichloride, cyclopentadienyl dimethoxy titanium chloride, Pentamethylcyclopentadienyl methoxy titanium dichloride, cyclopentadienyl tribenzyl titanium, pentamethylcyclopentadienyl methyl diethoxy titanium, indenyl titanium trichloride, indenyl titanium trimethoxide, Indenyl CHITANTORI ethoxide, indenyl trimethyl titanium, indenyl tribenzyl titanium, etc. are mentioned.

[0018] moreover, as a bis(cyclopentadienyl) substitution product of the titanium compounds A screw Dimethyl titanium, a screw (Cyclopentadienyl) Diphenyl titanium, a screw (Cyclopentadienyl) Diethyl titanium, a screw (Cyclopentadienyl) Dibenzyl titanium, a screw (Cyclopentadienyl) Dimethyl titanium, a screw (Methylcyclopentadienyl) Dimethyl titanium, a screw (Pentamethylcyclopentadienyl) Dibenzyl titanium, a screw (Methyl dicyclopentadienyl) (Pentamethylcyclopentadienyl) Dibenzyl titanium, screw (pentamethylcyclopentadienyl) chloro methyl titanium, screw (pentamethylcyclopentadienyl) hydride methyl titanium, etc. are mentioned. Furthermore, the titanium compound containing the ligand of a bridge formation mold like ethylene screw (indenyl) dimethyl titanium, ethylene screw (tetrahydro indenyl) dimethyl titanium, and dimethyl silylene screw (cyclopentadienyl) dimethyl titanium is also mentioned. These transition-metals compounds may form a Lewis base and a complex. When there is the need of making high molecular weight of the styrene system polymer section among these titanium compounds, a titanium compound with an alkoxide and a permutation pi electron system ligand is desirable. Moreover, when making molecular weight low, a titanium compound with a pi electron system ligand and a halogen ligand is desirable.

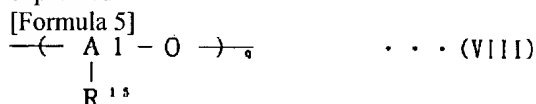
[0019] and as an example of a zirconium compound, among the transition-metals compounds expressed with said general formula (II)- (V) Cyclopentadienylzirconium trimethoxide, pentamethylcyclopentadienyl zirconium trimethoxide, cyclopentadienyl tribenzylzirconium, pentamethylcyclopentadienyl tribenzylzirconium, Bis-indenyl zirconium dichloride, zirconium dibenzyl dichloride, zirconium tetra-benzyl, TORIBUTOKISHI zirconium chloride, triisopropoxy zirconium chloride, etc. are mentioned. Furthermore, as an example of a hafnium compound, cyclopentadienyl hafnium trimethoxide, pentamethylcyclopentadienyl hafnium trimethoxide, a cyclopentadienyl tribenzyl hafnium, a pentamethylcyclopentadienyl tribenzyl hafnium, bis-indenyl hafnium dichloride, hafnium dibenzyl dichloride, hafnium tetra-benzyl, TORIBUTOKISHI hafnium chloride, triisopropoxy hafnium chloride, etc. are mentioned similarly. Moreover, as an example of a vanadium compound, vanadium trichloride, vanadyl trichloride, vanadium thoria cetyl acetate, vanadium tetra-chloride, vanadium tributoxide, vanadyl dichloride, vanadyl bisacetylacetate, vanadyl thoria cetyl acetate, etc. are mentioned similarly.

[0020] Next, the aluminum compound of the (B) component of a catalyst is the contact product of an organoaluminum compound and a condensing agent. here -- as an organoaluminum compound -- usually -- (general formula VI)  $\text{AlR}_3 \dots$  (VI) -- (R14 shows the alkyl group of carbon numbers 1-8 among a formula.) -- it is the organoaluminum compound expressed. Specifically, trialkylaluminums, such as trimethylaluminum, triethylaluminum, and triisobutylaluminum, are mentioned. In these, trimethylaluminum is desirable.

[0021] In addition, although water is typically mentioned about a condensing agent, various kinds of things, such as the water of adsorption to the arbitrary things in which the above-mentioned trialkylaluminum carries out a condensation reaction, for example, copper-sulfate 5 monohydrate, an inorganic substance, or the organic substance, are mentioned. As aluminosilane which is the (B) component of the catalyst used in this invention, there is a contact product of the trialkylaluminum expressed with said general formula (VI) as an organoaluminum compound and the water which is a condensing agent. Specifically, it is the following general formula (VII) [0022].



[0023] (-- among a formula, p shows polymerization degree and it is 0-50, and R15 shows the alkyl group of carbon numbers 1-8, and is a methyl group preferably.) -- the chain-like alkyl aluminosilane or the following general formula [0024] (VIII) expressed



[0025] (-- among a formula, q shows polymerization degree, and is 2-50, and R15 is the same as the above.) -- there is annular alkyl aluminosilane which has the repeat unit expressed.

[0026] Generally, the contact products of organoaluminum compounds, such as trialkylaluminum, and water are unreacted trialkylaluminum, the mixture of various kinds of condensation products, and the molecule with which these met intricately further in above-mentioned chain-like alkyl aluminosilane and annular alkyl aluminosilane, and these serve as various products according to the contact conditions of trialkylaluminum and the water which is a condensing agent. What is necessary is for there to be especially no definition in the reaction approach of the alkylaluminum compound in this case, and a condensing agent, and just to make it react to it according to well-known technique. For example, (i) In the approach and pan (iii) which dissolve the organoaluminum compound in the organic solvent, add the organoaluminum compound at the beginning at the

time of the approach of contacting this in water, and the (ii) polymerization, and add water behind There are water of crystallization contained in the metal salt etc., an approach to which the water of adsorption to an inorganic substance or the organic substance is made to react with an organoaluminium compound. In addition, although it goes on also under a non-solvent, it is desirable to carry out in a solvent and, as for this reaction, it can mention aromatic hydrocarbon, such as aliphatic hydrocarbon, such as a hexane, a heptane, and Deccan, or benzene, toluene, and a xylene, as a suitable solvent. And in the above-mentioned water, phosphorus compounds, such as sulfur compounds, such as amines, such as ammonia and ethylamine, and a hydrogen sulfide, and phosphite, etc. may contain about 20%.

[0027] When a hydrate etc. is used for the aluminosilicate (for example, alkyl aluminosilicate) of the (B) component which is the contact product of such an organoaluminium compound and a condensing agent after the above-mentioned catalytic reaction, solid-state residue is carried out a \*\* exception, in filtrate, under ordinary pressure or reduced pressure, it is 40-150 degrees C in temperature preferably, and it is effective the temperature of 30-200 degrees C and to heat-treat for 20 minutes to 8 hours, distilling off a solvent in 30 minutes - 5 hours preferably. Although what is necessary is just to define temperature suitably according to various kinds of situations in this heat treatment, it usually carries out in the above-mentioned range. Generally, if effectiveness is not discovered and it exceeds 200 degrees C at the temperature of less than 30 degrees C, the pyrolysis of alkyl aluminosilicate itself happens and neither is desirable. And a resultant is acquired in the state of a colorless solid-state or a solution according to the processing conditions of heat treatment. Thus, the need is accepted, and the obtained product can be dissolved or diluted with a hydrocarbon solvent, and can be used as a catalyst solution with it.

[0028] The suitable example of the aluminosilicate which is the contact product of the organoaluminium compound and condensing agent which are used as a (B) component of such a catalyst, especially alkyl aluminosilicate is the aluminum-methyl group observed by the proton nuclear-magnetic-resonance spectrum (aluminum-CH<sub>3</sub>). The high magnetic field component in the methyl proton signal field based on association is 50% or less of thing. That is, in the above-mentioned contact product, if the proton nuclear-magnetic-resonance (1 H-NMR) spectrum is observed under a room temperature and in a toluene solvent, the methyl proton signal based on "aluminum-CH<sub>3</sub>" will be seen in the range of 1.0--0.5ppm in tetramethylsilane (TMS) criteria. Since the proton signal (0 ppm) of TMS is in the methyl proton observation field based on "aluminum-CH<sub>3</sub>", The methyl proton signal based on this "aluminum-CH<sub>3</sub>" is measured on the basis of methyl proton signal 2.35ppm of the toluene in TMS criteria. A high magnetic field component the time of dividing into (namely, -0.1--0.5ppm) and other magnetic field components (namely, 1.0--0.1ppm) -- this high magnetic field component -- the whole -- 45 - 5% of thing can use it suitably as a (B) component of a catalyst preferably 50% or less.

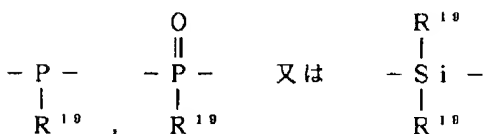
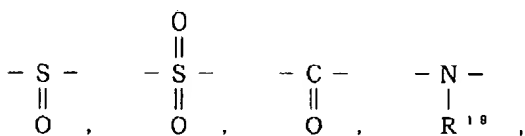
[0029] \*\* catalyst used in the approach of this invention can use the above (A) and the (B) component as a principal component, and can add other catalyst components (D) by the request other than the above further (\*\* catalyst). Catalytic activity can be remarkably raised by adding this catalyst component (D). here -- this catalyst component (D) -- the following (general formula IX) R<sub>16</sub>k AlY<sub>3-k</sub> [ ] ... (IX) (the inside of a formula, and R<sub>16</sub> -- carbon numbers 1-18 -- hydrocarbon groups, such as an alkyl group of 1-12, an alkenyl radical, an aryl group, an aralkyl radical, and an alkoxy group, and Y show a hydrogen atom or a halogen atom preferably.) k is the thing of the range of 1≤k≤3. It is the organoaluminium compound expressed. Specifically as an organoaluminium compound which is this (D) component, one sort, such as trimethylaluminum, triethylaluminum, triisobutylaluminum, dimethyl aluminum chloride, a diethylaluminum chloride, methyl aluminum dichloride, ethyl aluminum dichloride, and diethyl aluminum ethoxide, or two sorts or more can be mentioned. Moreover, it sets in the range which does not spoil stereoregularity and is a general formula (X).

W-R<sub>17</sub>(P) r-R<sub>18</sub>-W' ... (X)

Among [type, the hydrocarbon group of carbon numbers 1-20 and carbon numbers 7-30 carry out the permutation aromatic hydrocarbon radical of R<sub>17</sub> and R<sub>18</sub>, \*\*\*\* shows the permutation aromatic hydrocarbon radical of the carbon numbers 6-40 which have a substituent containing hetero atoms, such as oxygen, nitrogen, and sulfur, and P is the hydrocarbon group of carbon numbers 1-20, and [0030].

[Formula 6]

- O -, - S -, - S - S -,



[0031] (-- R<sub>19</sub> is a hydrogen atom or the hydrocarbon group of carbon numbers 1-6.) -- it is shown, W and W' shows a hydroxyl group, an aldehyde group, and a carboxyl group, and r shows the integer of 0, or 1-5. ] The organic compound which comes out and has at least two hydroxyl groups or aldehyde group expressed, and a carboxyl group can be added. as the example of an organic compound expressed with the above-mentioned general formula (X) -- for example -- 2,

2'-hydroxy-3, and 3' - G t-butyl -5, 5'-dimethyl diphenyl sulfide; 2, and 2' - hydroxy-3 and 3' - G t-butyl -5 and 5' - dimethyl diphenyl ether etc. is mentioned.

[0032] In using \*\* catalyst which uses the above (A) and the (B) component as a principal component in the approach of this invention The rate of each [ these ] component changes with the class of each component, the class of styrene system monomer which is a raw material, or other conditions. although not set uniquely -- usually -- as the ratio (mole ratio), i.e., aluminum/transition metals, of the aluminum in the (B) component, and the transition metals in the (A) component (for example, titanium) -- 1-106 -- desirable -- 10-104 it is . as a ratio with the aluminum in the aluminosilane which is usually the (B) component of a styrene system monomer and a catalyst although what is necessary is just to define the operating rate of a raw material monomer and a catalyst suitably, i.e., a styrene system monomer / aluminum, (mole ratio) -- 1-106 -- desirable -- 102-106 it is .

[0033] By the approach of this invention, \*\* catalyst, i.e., the catalyst which uses as a principal component the compound which reacts with said transition-metals compound as the aforementioned (A) component and a (C) component, and forms the complex of ionicity, can be used. As a compound which reacts with said transition-metals compound of this (C) component, and forms the complex of ionicity Although the class is not necessarily restricted, as a desirable thing A cation and two or more radicals are a periodic table VB group and VIB. A group, a VIIB group, a VIII group, IB group, and IIB A group, an IIIA group, and IVA The coordinated complex compound which consists of an anion combined with the element chosen from the group and VA group is mentioned. In addition, by the approach of this invention, \*\* catalyst which uses the aforementioned (A) component, the (C) component, and the (D) component as a principal component can be used. Here, as a transition-metals compound which is the (A) component, although what is necessary is just to select from the above mentioned thing suitably, they are the aforementioned general formula (II), (III), and (IV) preferably. And what is necessary is just to use the transition-metals compound expressed with (V). Furthermore, the compound which has at least one or more aryl groups of carbon numbers 6-20 is good preferably. And although what is necessary is just to select from inside suitably also about the organoaluminum compound which is the (D) component although described above, it is good to use what is preferably expressed with a general formula (IX).

[0034] although the class is not necessarily restricted as a (C) component here -- the following general formula (XI) -- or (XII) The coordinated complex compound expressed can be used suitably.

$v ([L1-H] u+) i ([M 5X1X2 \dots Xs] (second-t) -) \dots (XI) \text{ or } - ([L2] u+) v ([M6 X1 X2 \dots Xs] (second-t) -) i \dots (XII) \text{ -- [ --}$   
 however, L2 is M7, R20R21M8, or R223 C. ] For the inside of [type, and L1, a Lewis base, M5, and M6 are VB group of the periodic table, a VIB group, a VIIB group, a VIII group, IB group, an IIB group, an IIIA group, and IVA, respectively. The element chosen from the group or VA group, M7 IB group of the periodic table, and IIB The metal chosen from the group and the VIII group, M8 The metal chosen from the VIII group of a periodic table, and X1 -Xs, respectively A hydrogen atom, a dialkylamino radical, an alkoxy group, an aryloxy group, the alkyl group of carbon numbers 1-20, The aryl group, the alkyl aryl radical, the arylated alkyl radical, the permutation alkyl group, the organic metalloid radical, or halogen atom of carbon numbers 6-20 is shown. As for a cyclopentadienyl group, a substituent cyclopentadienyl group, an indenyl group or a fluorenyl group, and R22, R20 and R21 show a hydrocarbon group, respectively. t is M5 and M6. For the integer of 1-7, and s, the integer of 2-8 and u are L1-H and L2 at a valence. The integer of 1-7 and v are one or more integers and  $i=uxv/(second-y)$  in an ionic valence. ] It is the compound come out of and expressed.

[0035] Above L1 As an example of a Lewis base shown Ether, such as wood ether, diethylether, and a tetrahydrofuran, Ester, such as thioether, such as tetrahydrothiophene, and ethyl benzoate Amines, such as a nitril [ , such as an acetonitrile and a benzonitrile, ], trimethylamine, triethylamine, tributylamine, N,N-dimethylaniline, 2, and 2'-bipyridine and a phenanthroline, Phosphines, such as a triethyl phosphine and triphenyl phosphine As chain-like unsaturated hydrocarbon, ethylene, a butadiene, 1-pentene, an isoprene, pentadiene, 1-hexenes, and these derivatives, Benzene, toluene, a xylene, cycloheptatriene, cyclo-octadiene, cyclooctatriene, cyclo-octatriene, these derivatives, etc. are mentioned as annular unsaturated hydrocarbon. M5 and M6 As an example, it is M8 as examples of M7, such as B, aluminum, Si, P, As, and Sb, such as Li, Na, Ag, and Cu. Fe, Co, nickel, etc. are mentioned as an example. X1 - Xs as an example -- as for example, a dialkylamino radical -- a dimethylamino radical and a diethylamino radical -- As an alkoxy group, as a methoxy group, an ethoxy radical, an n-butoxy radical, and an aryloxy group A phenoxy group, 2, 6-dimethyl phenoxy group, a naphthyloxy radical, As an alkyl group of carbon numbers 1-20, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, n-octyl radical, a 2-ethylhexyl radical, As the aryl group, alkyl aryl radical, or arylated alkyl radical of carbon numbers 6-20 A phenyl group, p-tolyl group, benzyl, a pentafluorophenyl radical, 3, 5-JI (trifluoromethyl) phenyl group, 4-tertiary butylphenyl radical, 2, 6-dimethylphenyl radical, 3, 5-dimethylphenyl radical, 2, 4-dimethylphenyl radical, 1, A 5 methyl antimony radical, a trimethylsilyl radical, a trimethyl gel mill radical, a diphenyl arsine radical, a dicyclohexyl antimony radical, and a diphenyl boron radical are mentioned as F, Cl, Br, I, and an organic metalloid radical as 2-dimethylphenyl radical and a halogen. As an example of the substituent cyclopentadienyl group of R20 and R21, a methylcyclopentadienyl radical, a butylcyclopentadienyl radical, and a pentamethylcyclopentadienyl group are mentioned.

[0036] Said general formula (XI) (XII), Specifically in a compound, the following can be used especially suitably. for example, as a compound of a general formula (XI) Tetra-phenyl triethyl borate ammonium, tetra-phenyl boric acid TORIPURO pill ammonium, tetra-phenyl boric acid Tori (n-butyl) ammonium, tetrakis (o, p-dimethylphenyl) boric acid Tori (n-butyl) ammonium, Tetra-phenyl boric acid trimethylammonium, tetrakis Boric acid Tori (p-trifluoromethyl) Ammonium, (n-butyl) Tetra-phenyl boric acid triphenyl phosphonium, tetra-phenyl boric acid Tori (methylphenyl) phosphonium, tetra-phenyl boric acid tris (dimethylphenyl) phosphonium, tetrakis (pentafluorophenyl) boric acid i-propyl ammonium,



Tetra-phenyl boric acid dicyclohexyl ammonium, tetrakis Triethyl borate ammonium, tetrakis (pentafluorophenyl) boric acid Tori (n-butyl) ammonium, hexafluoro arsenic acid triethyl ammonium, tetrakis (pentafluorophenyl) boric acid dimethyl anilinium, (Pentafluorophenyl) Tetrakis Boric acid diethyl anilinium, (Pentafluorophenyl) There is tetrakis (pentafluorophenyl) boric acid di-n-butyl anilinium, tetrakis (pentafluorophenyl) methyl borate diphenyl ammonium, tetrakis (pentafluorophenyl) boric acid p-BUOMO-N, and N-dimethyl anilinium etc.

[0037] On the other hand, it is a general formula (XII). As a compound Tetra-phenyl boric acid ferro SENIUMU, tetrakis Boric acid ferro SENIUMU, tetrakis (Pentafluorophenyl) Boric acid decamethyl ferro SENIUMU, (Pentafluorophenyl) Tetrakis Boric acid acetyl ferro SENIUMU, tetrakis (pentafluorophenyl) boric acid formyl ferro SENIUMU, tetrakis (pentafluorophenyl) boric acid cyano ferro SENIUMU, tetra-phenyl boric acid silver, tetrakis (Pentafluorophenyl) (Pentafluorophenyl) There are boric acid silver, tetra-phenyl boric acid trityl, tetrakis (pentafluorophenyl) boric acid trityl, hexafluoro arsenic \*\*\*\*, hexafluoro antimonioic acid silver, tetrafluoroboric silver, etc.

[0038] The catalyst used by the approach of this invention has some which there is another thing which uses \*\* (A) component and the (C) component as a principal component although what uses the aforementioned \*\* (A) component and the (B) component as a principal component, \*\* (A) component, the (B) component, and the (D) component are used as a principal component, and use \*\* (A) component, the (C) component, and the (D) component as a principal component as other modes In this case, although especially the addition rate of the (A) component and the (C) component is not limited, it is desirable 1:0.01-1:100 and to carry out the mole ratio of a (A) component:(C) component to especially 1:1-1:10. Furthermore, the (A) component and the (C) component are contacted beforehand, and the obtained contact product may be used for them, separating and washing it, and they may be contacted within a polymerization system. Moreover, the amount of the (D) component used is usually 0-100 mols to one mol of (A) components. (D) If a component is used, improvement in polymerization activity can be aimed at, but even if many [ not much ], don't discover the effectiveness equivalent to an addition. In addition, the (D) component may be contacted to the contact product of the (A) component, the (C) component or the (A) component, and the (C) component, and may be used. This contact may be contacted beforehand, and sequential addition may be carried out and it may make it contact into a polymerization system. And for the amount of the (C) component used, a raw material monomer / complexing nature compound (mole ratio) is 1-109, especially 100-107. Becoming is desirable.

[0039] The approach of this invention carries out the polymerization (\*\*) of said styrene system monomer under existence of the catalyst of either \*\* - \*\* first in the solution of a polymerization or the thermoplastic polymer which dissolved the thermoplastic polymer in the dissolution or a hydrocarbon system solvent in the (\*\*) polymerization at the styrene system monomer of a raw material although it copolymerized, and prepares a polystyrene system resin constituent. Consequently, the polystyrene system resin constituent excellent in homogeneity dispersibility can be obtained. (\*\*) Unless the thermoplastic polymer is dissolving in the styrene system monomer or the hydrocarbon system solvent at the polymerization reaction system, the polystyrene system resin constituent obtained will not be able to become uneven, and the object cannot be attained. Here, there are various things as a thermoplastic polymer used for obtaining the polystyrene system resin constituent excellent in homogeneity dispersibility, and if it dissolves in the thing and hydrocarbon system solvent which dissolve in a styrene system monomer, there will be especially no limit. For example, what is illustrated below can be used. As poly norbornene system resin, first, specifically Poly norbornene, Pori (5-methyl norbornene), Pori (5-ethyl norbornene), Pori (5-propyl norbornene), Pori (5, 6-dimethyl norbornene), Pori (1-methyl norbornene), Pori (7-methyl norbornene), Pori (5, 5, 6-trimethyl norbornene), Pori (5-phenyl norbornene), Pori (5-benzyl norbornene), Pori (5-ethylidene norbornene), Pori (5-vinyl norbornene), Pori (1, 4, 5, 8-dimethano - 1, 2, 3, 4,a [ 4 ], 5, 8, and 8a-octahydronaphthalene), Pori (2-methyl - 1, 4, 5, 8-dimethano - 1, 2, 3, 4,a [ 4 ], 5, 8, and 8a-octahydronaphthalene), Pori (2-ethyl - 1, 4, 5, 8-dimethano - 1, 2, 3, 4,a [ 4 ], 5, 8, and 8a-octahydronaphthalene), Pori (2, 3-dimethyl - 1, 4, 5, 8-dimethano - 1, 2, 3, 4,a [ 4 ], 5, 8, and 8a-octahydronaphthalene), Pori (1, 2-dihydrodicyclopentadiene), Pori (5-chloro norbornene), Pori (5 and 5-dichloro norbornene), Pori (5-fluoro norbornene), Pori (5, 5, 6-trifluoro-6-trifluoromethyl norbornene), Pori (5-chloro methyl norbornene), Pori (5-methoxy norbornene), Pori (5-dimethylamino norbornene), Pori (5-cyano norbornene), etc. are mentioned. Furthermore, polyolefines and these copolymers, such as polyethylene, a polypropylene bilene, and polybutene, can be used. And even if such polyolefines are contained, it does not interfere with the above-mentioned poly norbornene system resin.

[0040] moreover, as polystyrene system resin as a thermoplastic polymer For example, atactic polystyrene and isotactic polystyrene are begun. The polymer of alpha-permutation styrene, such as alpha methyl styrene, alpha-ethyl styrene, and alpha-phenyl styrene (diphenyl styrene), 4-vinyl biphenyl; -- 3-vinyl biphenyl; -- the polymer of vinyl biphenyls, such as 2-vinyl biphenyl, -- 1- (4-vinyl phenyl)-naphthalene; 2- (4-vinyl phenyl)-naphthalene; -- 1-(3-vinyl phenyl)-naphthalene; -- 2-(3-vinyl phenyl)-naphthalene; -- 1-(2-vinyl phenyl)-naphthalene; -- the polymer of vinyl phenyl naphthalene, such as 2-(2-vinyl phenyl) naphthalene, -- 1- (4-vinyl phenyl)-anthracene; 2- (4-vinyl phenyl)-anthracene; 9- (4-vinyl phenyl)-anthracene; 1- (3-vinyl phenyl)-anthracene; 2- (3-vinyl phenyl)-anthracene; 9- (3-vinyl phenyl)-anthracene; -- 1-(2-vinyl phenyl)-anthracene; -- 2-(2-vinyl phenyl)-anthracene; -- the polymer of vinyl phenyl anthracene, such as a 9-(2-vinyl phenyl)-anthracene, -- 1- (4-vinyl phenyl)-phenanthrene; 2- (4-vinyl phenyl)-phenanthrene; 3- (4-vinyl phenyl)-phenanthrene; 4- (4-vinyl phenyl)-phenanthrene; 9- (4-vinyl phenyl)-phenanthrene; 1- (3-vinyl phenyl)-phenanthrene; 2- (3-vinyl phenyl)-phenanthrene; 3- (3-vinyl phenyl)-phenanthrene; 4- (3-vinyl phenyl)-phenanthrene; 9- (3-vinyl phenyl)-phenanthrene; 1- (2-vinyl phenyl)-phenanthrene; 2- (2-vinyl phenyl)-phenanthrene; -- 3-(2-vinyl phenyl)-phenanthrene; -- 4-(2-vinyl phenyl)-phenanthrene; -- the polymer of vinyl phenyl phenanthrenes, such as a 9-(2-vinyl



phenyl)-phenanthrene, -- 1-(4-vinyl phenyl)-pyrene; 2-(4-vinyl phenyl)-pyrene; -- 1-(3-vinyl phenyl)-pyrene; -- 2-(3-vinyl phenyl)-pyrene; -- 1-(2-vinyl phenyl)-pyrene; -- the polymer of vinyl phenyl pyrenes, such as a 2-(2-vinyl phenyl)-pyrene, -- 4-vinyl-p-terphenyl; 4-vinyl-m-terphenyl; 4-vinyl-o-terphenyl; 3-vinyl-p-terphenyl; -- 3-vinyl-m-terphenyl; -- 3-vinyl-o-terphenyl; -- 2-vinyl-p-terphenyl; -- 2-vinyl-m-terphenyl; -- the polymer of vinyl terphenyl, such as 2-vinyl-o-terphenyl, -- The polymer of vinyl phenyl terphenyl, such as 4-(4-vinyl phenyl)-p-terphenyl, 4-vinyl-4'-methyl biphenyl; -- 4-vinyl-3' - methyl biphenyl; -- 4-vinyl-2' - methyl biphenyl; -- 2-methyl-4-vinyl biphenyl; -- the polymer of vinyl alkyl biphenyls, such as a 3-methyl-4-vinyl biphenyl, -- 4-vinyl-4'-fluoro biphenyl; 4-vinyl-3'-fluoro biphenyl; 4-vinyl-2'-fluoro biphenyl; 4-vinyl-2-fluoro biphenyl; 4-vinyl-3-fluoro biphenyl; 4-vinyl-4'-chloro biphenyl; 4-vinyl-3'-chloro biphenyl; 4-vinyl-2'-chloro biphenyl; 4-vinyl-2-chloro biphenyl; 4-vinyl-3-chloro biphenyl; 4-vinyl-4'-BUROMO biphenyl; -- 4-vinyl-3' - BUROMO biphenyl; -- 4-vinyl-2' - BUROMO biphenyl; -- 4-vinyl-2-BUROMO biphenyl; -- the polymer of halogenation vinyl biphenyls, such as a 4-vinyl-3-BUROMO biphenyl, -- The polymer of trialkylsilyl vinyl biphenyls, such as a 4-vinyl-4'-trimethylsilyl biphenyl, 4-vinyl-4'-trimethyl SUTAN nil biphenyl; The polymer of trialkyl SUTANNIRU vinyl biphenyls, such as a 4-vinyl-4'-tributylstannyl biphenyl, The polymer of trialkylsilyl methylvinyl biphenyls, such as a 4-vinyl-4'-trimethylsilylmethyl biphenyl, 4-vinyl-4'-trimethyl SUTANNIRU methyl biphenyl; styrene system polymers, such as a polymer of trialkyl SUTANNIRU methylvinyl biphenyls, such as a 4-vinyl-4'-tributylstannyl methyl biphenyl, and a polymer of an acenaphthylene, are mentioned.

[0041] And as polymaleimide system resin, N-permutation maleimide polymers, such as N-methyl maleimide, N-ethyl maleimide, N-phenyl maleimide, N-(2-FURORU phenyl) maleimide, N-(2-methylphenyl) maleimide, N-(2, 6-dimethylphenyl) maleimide, N-(cyclohexyl) maleimide, N-(4-hydroxyphenyl) maleimide, and N-(4-carboxyphenyl) maleimide, etc. are mentioned, for example.

[0042] Even if each aforementioned thermoplastic polymer is a copolymer which consists of rates of arbitration, it does not interfere. Moreover, it is satisfactory although the resinous principle which consists of an acrylate system monomer or a methacrylate system monomer is included in these polymers or a copolymer in the range which does not spoil the activity of the above-mentioned catalyst. What is necessary is to carry out the polymerization (\*\*) of said each of these thermoplastic polymers in the solution of the thermoplastic polymer which dissolved in the styrene system monomer or the hydrocarbon system solvent in carrying out the polymerization (\*\*) of the styrene system monomer, but just to define suitably the rate of the thermoplastic polymer contained in a polystyrene system resin constituent according to various situations. Usually, 0.1 to 60% of the weight, the rate contained in the resin constituent obtained is preferably set up 0.1 to 40% of the weight so that it may become 0.1 - 20% of the weight preferably especially. Consequently, the polystyrene system resin constituent with which a principal chain is mainly concerned with the styrene system polymer of syndiotactic structure can be obtained. Make it dissolve in a styrene system monomer, or select a meltable solvent out of a hydrocarbon system solvent, for example, aliphatic hydrocarbon, alicyclic hydrocarbon, or aromatic hydrocarbon, it is made to dissolve in advance in an activity, and said thermoplastic polymer fully removes impure parts, such as moisture, is saved under inactive air currents, such as an argon and nitrogen, and is used suitably. Here, as a solvent in which a thermoplastic polymer is dissolved, alicyclic hydrocarbon, such as alicyclic hydrocarbon, such as aliphatic hydrocarbon, such as a pentane, a hexane, a heptane, and an octane, a cyclopentane, a cyclohexane, and a methylcyclohexane, or benzene, toluene, a xylene, and ethylbenzene, is mentioned, for example.

[0043] In order to manufacture a polystyrene system resin constituent by the approach of this invention, as mentioned above, the polymerization (\*\*) of said styrene system monomer is carried out in the solution which dissolved said thermoplastic polymer in styrene or a solvent under existence of either said catalyst \*\* - \*\*. What is necessary is to be 10-80 degrees C preferably, and just to select polymerization time amount in 1 - 10 hours the polymerization temperature of 0-120 degrees C, generally, although what is necessary is just to select [ polymerization / (\*\*) / of said styrene system monomer ] suitably about polymerization temperature, polymerization time amount, and a polymerization method. (\*\*) As a polymerization method, both a bulk polymerization solution polymerization and a suspension polymerization may be possible, and it may be any of a continuation polymerization and a discontinuous polymerization. Here, if it is in solution polymerization, even if it can use aliphatic hydrocarbon, such as alicyclic hydrocarbon, such as aromatic hydrocarbon, such as the same benzene as the solvent used as a solvent when dissolving said thermoplastic polymer, toluene, a xylene, and ethylbenzene, a cyclopentane, a cyclohexane, and a methylcyclohexane, a pentane, a hexane, a heptane, and an octane, etc. or uses other solvents, it does not interfere. In these, aliphatic hydrocarbon and aromatic hydrocarbon are desirable. In this case, a monomer/solvent (volume ratio) can be chosen as arbitration. And what is necessary is just to perform the molecular weight control or presentation control of a polymer obtained (\*\*) by the approach usually used. Molecular weight control is (i). Hydrogen and (ii) temperature (iii), It is controllable by monomer concentration etc. moreover, presentation control -- for example, (i) monomer brewing -- it is possible at modification of a ratio, selection of (ii) catalyst kind, etc.

[0044] The styrene system (\*\*) polymer manufactured by the approach of this invention can obtain that in which the stereoregularity has syndiotactic structure by carrying out a polymerization (\*\*) under existence of said catalyst. To the principal chain with which stereochemistry structure is formed from syndiotactic structure, i.e., carbon-carbon bonding, the phenyl group which is a side chain, and a permutation phenyl group have the spacial configuration located in an opposite direction by turns, and, as for syndiotactic structure, a quantum is carried out here with the nuclear magnetic resonance method (the 13 C-NMR method) according [ the tacticity ] to isotope carbon. In the abundance of two or more configuration units which the tacticity measured by the 13 C-NMR method follows, for example, two cases, die ADDO and three cases can show TORIADDO and five cases by the pentad. The styrene system (\*\*) polymer which has the syndiotactic structure told to this invention shows preferably what has 50% or more of syndiotacticity more preferably 30% or more preferably [ it is more

desirable and ] 75% or more by racemic die ADDO in the chain of a styrene system repeating unit at 85% or more or a raceme pentad. However, the degree of syndiotacticity is changed a little according to the class of substituent etc. Although the molecular weight of the polymer obtained by the manufacture approach of this invention (\*\*) changes according to polymerization conditions, it is usually 5000-4,500,000 in weight average molecular weight. They are 10,000 or more things preferably. And the glass transition temperature of the styrene system (\*\*) polymer which has the syndiotactic structure acquired by doing in this way is 96 degrees C or more. In this invention, since a polymerization (\*\*) is carried out in the polymerization (\*\*) of a styrene system monomer in the solution made to dissolve said thermoplastic polymer in styrene or a solvent, the styrene system (\*\*) polymer and the thermoplastic polymer which have syndiotactic structure are distributed by homogeneity. As reduced viscosity (viscosity with a concentration of 0.05g [deciliter] measured at 135 degrees C among 1,2,4-trichlorobenzene) of the styrene resin constituent currently distributed by this homogeneity, 0.2-20 deciliters /are [ g ] 0.5-10 deciliters/g preferably.

[0045] Thus, subsequently the obtained polystyrene system resin constituent is fabricated by the approach usually enforced. And the acquired Plastic solid can manufacture efficiently the porosity-sized polystyrene system porosity (separation) ingredient by removing said thermoplastic polymer currently distributed to homogeneity from a polystyrene system resin constituent. In order to remove a thermoplastic polymer from a Plastic solid, the well-known technique usually enforced is applicable. For example, what is necessary is to make it an extract, washing and extraction, or a gas using the hydrocarbon system solvent which dissolves this thermoplastic polymer, and for there to be various approaches, such as spraying a solvent, and just to apply suitably. In addition, it is not necessary to necessarily remove the clearance from the Plastic solid of a thermoplastic polymer 100% in this case that what is necessary is just to porosity-size. In addition, kneading etc. can also be pretreated before fabricating using a polystyrene system resin constituent. Altitude can be made to distribute a thermoplastic polymer more by this processing. This kneading is usually performed by the melting kneading methods, such as a Banbury mixer, a monopodium or a twin screw extruder, a kneader, and a roll mill. And on the occasion of porosity-izing, there is especially no limit in the configuration, and especially thin Plastic solids, such as a filmy material, a film, a sheet, a pipe, a filament, and a hollow filament, are suitable. Furthermore, if a polystyrene system resin constituent is porosity-sized by fabricating to a particle (the shape of a bead), it is crystallinity and can also obtain the porosity bead excellent in thermal resistance and solvent resistance.

[0046]

[Example] Next, an example and the example of a comparison explain this invention in more detail. In addition, this invention is not restricted at all by the following example.

17.7g (CuSO<sub>4</sub> and 5H<sub>2</sub>O) (71 millimol) of 200ml [ of toluene ] and copper-sulfate 5 monohydrates and 24ml (250 millimol) of trimethylaluminums were put into the glass container of 500ml of content volume in which example 1 (1) methyl aluminoxane carried out the preparation nitrogen purge, and it was made to react to it at 40 degrees C for 8 hours. Then, reduced pressure distilling off of the toluene was carried out further, and 6.7g (methyl aluminoxane) of catalyst products was obtained from the solution which removed the solid-state component and was obtained. The molecular weight measured with the cryoscopic method of this thing was 610. Moreover, it is based on JP,62-325391,A. If the proton nuclear-magnetic-resonance spectrum is observed in the high magnetic field component by 1 H-NMR measurement, i.e., the bottom toluene solution of a room temperature, the methyl proton signal based on "aluminum-CH<sub>3</sub>" association will be seen in the range of 1.0--0.5ppm in tetramethylsilane criteria. Since the proton signal (0 ppm) of a tetramethylsilane is in the observation field based on the methyl proton based on "aluminum-CH<sub>3</sub>" association, The methyl proton signal based on this "aluminum-CH<sub>3</sub>" association is measured on the basis of methyl proton signal 2.35ppm of the toluene in tetramethylsilane criteria. When it divided into a high magnetic field component (namely, -0.1--0.5ppm) and other magnetic field components (namely, 1.0--0.1ppm), this high magnetic field component was 43% of the whole.

(2) Pori (norbornene) 20g was dissolved in 200ml of toluene, the toluene solution of Pori (norbornene) was prepared, using Pori (norbornene) ([eta] =1.94 deciliter/g) as a preparation thermoplasticity polymer of a thermoplastic polymer content solution, and it saved under the nitrogen air current.

(3) Nitrogen fully permuted the reaction container with an agitator of 1.0l. of manufacture content volume of a polystyrene system resin constituent. After heating at 70 degrees C, the toluene solution of Pori (norbornene) prepared by 80ml of dry toluene, 420ml of styrene, and (2) was added, triisobutylaluminum (TIBA) 10 millimol and methyl aluminoxane 10 millimol obtained by (1) were added as a catalyst, and it stirred for 30 minutes. Subsequently, 50 micromole \*\*\*\* and a polymerization reaction were performed for 1, 2, 3, 4, and 5-pentamethylcyclopentadienyl titanium trimethoxide for 6 hours. Then, a methanol is poured in, the reaction was stopped, after filtration, the acid methanol was poured in further, the polymerization object was washed, and the catalyst component was decomposed. It was made to dry under reduced pressure and the 120g polystyrene system resin constituent was obtained. About this resin constituent, differential scan heat measurement (DSC) and nuclear-magnetic-resonance spectrum measurement (NMR) were performed.

(a) As a result of measuring by DSC-II by measurement PerkinElmer, Inc. by DSC, the melting point (Tm) was 268 degrees C, and glass transition temperature (Tg) was 101 degrees C.

(b) As a result of measuring measurement 13 C-NMR by NMR, it is the ring C1 of a styrene chain. A carbon signal It was observed by 145.1 ppm. It has checked that the spacial configuration of obtained SPS had syndiotactic structure from this signal. And the syndiotacticity in the raceme pentad of this SPS was 94%. Moreover, the content of Pori (norbornene) was 16.7 % of the weight.

(4) Thermoforming of the polystyrene system resin constituent obtained by manufacture (3) of a porous sheet was carried out

to the shape of a 5.0cmx5.0cmx0.05cm sheet with the molding temperature of 300 degrees C, and the test piece was produced. Subsequently, after it performed 80 degrees C and washing of 4 hours and the methanol fully washed the test piece using the good solvent (toluene) of the thermoplastic polymer used at the time of manufacture of a polystyrene system resin constituent, 90 degrees C and desiccation of 8 hours were performed. Furthermore, it heated for 20 minutes at 150 degrees C, and under the usual conditions, it exposed to air, annealing processing was cooled and carried out to the room temperature, and the porous sheet was manufactured.

[0047] It replaced with Pori (norbornene) of example 2 example 1, and carried out like the example 1 except having used Pori (alpha methyl styrene) 10g. The yield of a polystyrene system resin constituent was [ 100 degrees C and Tm of 105g and Tg ] 267 degrees C. And the syndiotacticity in the raceme pentad measured by 13 C-NMR was 93%. Moreover, the content of Pori (alpha methyl styrene) was 9.5 % of the weight.

[0048] It replaced with Pori (norbornene) of example 3 example 1, and carried out like the example 1 except having used Pori [N-(4-KURORU phenyl) maleimide] 8g. The yield of a polystyrene system resin constituent was [ 99 degrees C and Tm of 99g and Tg ] 268 degrees C. And the syndiotacticity in the raceme pentad measured by 13 C-NMR was 93%. Moreover, the content of Pori [N-(4-KURORU phenyl) maleimide] was 6.5 % of the weight.

[0049] In example 4 example 1, it carried out like the example 1 except having changed into the catalyst which consists of triisobutylaluminum 30 micromole, tetrapod (pentafluorophenyl) boric-acid triethyl ammonium 5 micromole; 1, 2, 3 and 4, and 5-pentamethylcyclopentadienyl titanium trimethyl 5 micromole as a polymerization catalyst. The yield of a polystyrene system resin constituent was [ 100 degrees C and Tm of 132g and Tg ] 269 degrees C. And the syndiotacticity in the raceme pentad measured by 13 C-NMR was 95%. Moreover, the content of Pori (norbornene) was 14 % of the weight.

[0050] In example 5 example 4, it replaced with Pori (norbornene) and carried out like the example 4 except having used Pori [N-(cyclohexyl) maleimide] 10g. The yield of a polystyrene system resin constituent was [ 98 degrees C and Tm of 123g and Tg ] 270 degrees C. And the syndiotacticity in the raceme pentad measured by 13 C-NMR was 96%. Moreover, the content of Pori [N-(cyclohexyl) maleimide] was 7.5 % of the weight.

[0051] Methyl aluminoxane 3 millimol obtained by triisobutylaluminum 3 millimol and example 1-(1) as a catalyst with 80ml of toluene, and 420ml of styrene using the same reactor as the example example 1 of reference; the polymerization reaction was performed at 70 degrees C for 4 hours using the catalyst which consists of 1, 2, 3, 4, and 5-pentamethylcyclopentadienyl titanium trimethoxide 15 micromole. Processing after a polymerization reaction was made to be the same as that of an example 1. The yield of polystyrene (SPS) was 161g, Tg was 95 degrees C, and Tm was 270 degrees C. And the syndiotacticity in the raceme pentad measured by 13 C-NMR was 98%.

[0052] Mixed preparation of SPS [ which was obtained in the example 1 of a comparison - the example of 3 reference ], Pori which was used in the examples 1, 2, and 5 ] (norbornene), Pori (alpha methyl styrene), and Pori [N-(cyclohexyl) maleimide] was carried out so that it might become the same weight composition as the polystyrene system resin constituent obtained in the examples 1, 2, and 5, respectively. Hereafter, it carried out like the example 1.

SPS obtained in the example of example of comparison 4 reference was used as the polystyrene system resin constituent. Hereafter, it carried out like the example 1.

It prepared on the same conditions as the example in an example of comparison 5 JP,2-4840,A description, and considered as the polystyrene system resin constituent. Hereafter, it carried out like the example 1.

[0053] Reduced viscosity was measured about the polystyrene system resin constituent obtained in the example and the example of a comparison. Moreover, as the performance evaluation, using the polystyrene system resin constituent obtained in each example and the example of a comparison, it kneaded for 8 minutes, and the strand was fabricated by extrusion after that, and injection molding was performed at 300 degrees C, the test piece was created, and 280 degrees C of heat deflection temperature were measured with the small making machine (the product made from Custom Scientific Instrument Inc: Model CS-183). The result is shown in the 1st table. And about the strand of examples 1, 2, and 3, the electron microscope photograph (x10,000) was taken and the fracture surface was shown in drawing 1 -3. In addition, although it was going to knead with the above-mentioned small making machine and was going to fabricate the strand by extrusion after that about the polystyrene system resin constituent of the examples 1-3 of a comparison, it was not able to fabricate because of poor kneading.

[0054]

[A table 1]

第 1 表

	スチレン		触媒系	熱可塑性重合体	
	種 類	使用量 (ml)		種 類	添加量 (g)
実施例 1	スチレン	4 2 0	(I)	PNB	2 0
実施例 2	スチレン	4 2 0	(I)	PMS	1 0
実施例 3	スチレン	4 2 0	(I)	PCPMI	8
実施例 4	スチレン	4 2 0	(II)	PNB	2 0
実施例 5	スチレン	4 2 0	(II)	PCHMI	1 0
比較例 1	P S	8. 3	—	PNB	1. 7
比較例 2	P S	8. 1	—	PMS	1. 9
比較例 3	P S	9. 2 5	—	PCHMI	0. 7 5
参考例	スチレン	4 2 0	(I)	—	—

比較例の P S 使用量：(g)

[0055]

[A table 2]

第 1 表 (続き①)

	収 量	添加樹脂 含量 (重量%)	還元粘度 (dl/g)	<sup>13</sup> C-NMR (%)
実施例 1	1 2 0	1 6. 7	3. 0 5	9 4
実施例 2	1 0 5	1 9. 0	2. 6 4	9 3
実施例 3	9 9	6. 5	2. 5 9	9 3
実施例 4	1 3 2	1 4. 0	2. 9 8	9 5
実施例 5	1 2 3	7. 5	2. 7 0	9 6
比較例 1	—	—	—	—
比較例 2	—	—	—	—
比較例 3	—	—	—	—
参考例	1 6 1	—	2. 0 1	9 8

[0056]

[A table 3]

第 1 表 (続き②)

	樹脂組成物		熱変形温度 (°C)
	T <sub>g</sub>	T <sub>m</sub>	
実施例 1	101	268	118.7
実施例 2	100	267	109.0
実施例 3	99	268	115.2
実施例 4	100	269	117.0
実施例 5	98	270	116.7
比較例 1	—	—	—
比較例 2	—	—	—
比較例 3	—	—	—
参考例	95	270	86.0

T<sub>g</sub>, T<sub>m</sub> : °C

[0057] In addition, each measurement followed the degree in the performance evaluation.

1) Reduced viscosity : among 1,2,4-trichlorobenzene, it carried out at cooling and \*\*30 degree C by part for 7-degree-C/to maintenance and \*\*30 degree C for 5 minutes, temperature up (second heating) was carried out by part for 20-degree-C/to maintenance and \*\*300 degree C for 5 minutes at viscosity 2 glass-transition-temperature (T<sub>g</sub>) melting out temperature (T<sub>m</sub>):Measuring condition \*\*300 degree C with a concentration of 0.05g [deciliter ] measured at 135 degrees C, and T<sub>g</sub> and T<sub>m</sub> were calculated at the time of second heating.

3) Syndiotacticity 4 heat deflection temperature in the raceme pentad computed from 13 C-NMR:13C-NMR : JIS Based on K-7207, the abbreviation in measurement and the 1st table is as follows.

PS: The polystyrene catalyst system manufactured in the example of reference: 1, 2, 3 and 4, and

5-pentamethylcyclopentadienyl titanium trimethoxide / methyl aluminoxane / triisobutylaluminum (II) 1, 2, 3, 4,

5-PENTAMECHIRUSHIKUROPENTAJIENIRUCHITANI UMUTORI methyl / tetrapod (pentafluorophenyl) boric-acid triethyl ammonium / triisobutylaluminum PNB: Pori (norbornene)

PMS: Pori (alpha methyl styrene)

PCPMI: Pori [N-(4-chlorophenyl) maleimide]

PCHMI: Pori [N-(cyclohexyl) maleimide]

[0058] Moreover, about the obtained porosity sheet, a water permeate flow and maintenance particle diameter were measured according to the conventional method. Moreover, the calorific value at the time of the fusion measured by DSC was measured. A measurement result is shown in the 2nd table.

[0059]

[A table 4]

第 2 表

	良溶媒	透過水量 (m <sup>3</sup> /m <sup>2</sup> ・d)	保持粒子径 (μm)	結晶部融解熱 (J/g)
実施例 1	トルエン	1.24	0.613	25.0
実施例 2	トルエン	1.55	0.762	25.7
実施例 3	N,N-ジメチル ホルムアミド	2.88	1.420	26.0
実施例 4	トルエン	1.44	0.711	26.3
実施例 5	トルエン	2.38	1.174	26.9
比較例 4	—	~0	~0	25.2
比較例 5	—	1.80	0.913	26.5

[0060] In addition, it sets to the 2nd table and a water permeate flow is the pressure of 0.492kg/cm<sup>2</sup>. It measured. Moreover, the crystal section heat of fusion was measured on the same conditions also in the 1st table, and measured the heat of fusion observed at the time of second heating.

[0061]

[Effect of the Invention] Since the polystyrene system resin constituent which the styrene system (\*\*) polymer (SPS) which has syndiotactic structure, and thermoplastics coalesce distributed to homogeneity in this invention is used like the above, the porosity polystyrene system ingredient obtained holds a mechanical property, chemical stability, etc. which are the advantage which SPS has, moreover is excellent in a thermal property, and further excellent in permeability. therefore, the porosity polystyrene system ingredient of this invention -- \*\*, such as ultrafiltration membrane, an ultraprecise filtration membrane, a reverse osmotic membrane, ion exchange membrane, a gas separation membrane, and permeable membrane, -- it is broadly used in various fields.

---

[Translation done.]